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Lattice dynamics and elastic properties of lanthanum monopnictides

Gökhan Gökoğlu [a,b,*], Aytaç Erkişi [c]

[a] Department of Physics, Karabük University, 78100 Karabük, Turkey
[b] Department of Physics, Bilkent University, 06800 Bilkent, Ankara, Turkey
[c] Department of Physics Engineering, Hacettepe University, 06800 Beytepe, Ankara, Turkey

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ABSTRACT

In this study, first principles calculation results of the second order elastic constants and lattice dynamics of two lanthanum monopnictides, LaN and LaBi, which crystallize in rock-salt structure (B1 phase), are presented. Calculations were based on plane wave basis sets and pseudopotential methods in the framework of Density Functional Theory (DFT) with generalized gradient approximation. Elastic constants are calculated by tetragonal and orthorhombic distortions on cubic structure. Phonon dispersion spectra was constructed in the linear response approach of the Density Functional Perturbation Theory (DFPT). The complete phonon softening with negative frequencies and large elastic anisotropy were observed for LaN single crystal as a sign of the structural instability. The phonon dispersion curve for LaBi is typical for lanthanum monopnictides and does not show any anomalous physical property. The calculated structural quantities for both LaN and LaBi systems agree well with the available experimental and theoretical data.

1. Introduction

The rare-earth monopnictides having no 4f electronic states are used as good references in order to understand the anomalous physical effects in other type of monopnictide compounds. These compounds crystallize in simple fcc rock salt structure with $Fm\bar{3}m$ crystallographic space group. The lanthanum monopnictides are very promising for this kind of applications and subject for investigation in various theoretical and experimental studies [1–5].

Electronic and structural aspects of rare-earth monopnictide compounds have been investigated in previous studies [6]. Structural phase transitions from NaCl structure (B1 phase) to body centered tetragonal and CsCl (B2) phase under high pressure are also studied extensively for several compounds [7–9]. Electronic band structure calculations of lanthanum monopnictides have started with the pioneering work of Hasegawa by self-consistent augmented plane wave (APW) method with local density approximation [10]. To date, electronic properties and lattice dynamics of most lanthanum pnictides have been studied by several groups. The structural phase transitions and some elastic parameters of rare-earth bismuthides were reported in a recent study [11]. But the works which specially focus on elastic properties are very rare, although there is a direct relation between elastic properties and vibrational dynamics.

In this work, we have studied the elastic and structural properties and lattice dynamics of LaN and LaBi systems in B1 phase using plane-wave pseudopotential method of the Density Functional Theory with GGA functionals. The vibrational properties were investigated in the linear response approach of the DFPT in which phonon frequencies can be obtained with more accuracy than the supercell approach. To our knowledge, there are only a few articles in the literature about the elastic properties of LaBi. The pnictogen atoms in the compositions under study, N and Bi, have the lowest and highest masses of the V–A group, respectively. This situation provides the possibility of investigating the effects of large mass difference on vibrational spectra.

2. Computational details

All cubic crystals have only three independent elastic constants due to high symmetry, namely C_{11}, C_{12} and C_{44}. The bulk modulus of the system can be expressed in terms of elastic constants;

$$B = (C_{11} + 2C_{12})/3, \quad (1)$$

which is the resistance of the material to a uniform hydrostatic pressure. Shear constant is defined as:

$$C_s = (C_{11} - C_{12})/2. \quad (2)$$

* Corresponding author at: Department of Physics, Karabük University, 78100 Karabük, Turkey. Tel.: +90 312 290 2151; fax: +90 312 266 4579.
E-mail address: ggokoglu@fen.bilkent.edu.tr (G. Gökoğlu).

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Bulk modulus of the system is calculated from the Vinet [12] equation of states:

$$E(V) = E(0) + \frac{9BV_0}{\xi^2}\{1 + \{\xi(1-x) - 1\}\exp\{\xi(1-x)\}\} \quad (3)$$

where $E(0)$ and V_0 are the zero pressure equilibrium energy and volume, respectively, $x = (\frac{V}{V_0})^{\frac{1}{3}}$ and $\xi = \frac{3}{2}(B' - 1)$, B is the bulk modulus and B' its pressure derivative.

Shear constant was calculated using the following volume conserving isochoric strain which produce a tetragonal distortion on original fcc rock-salt structure.

$$\epsilon = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & (1+\delta)^{-2} - 1 \end{pmatrix}, \quad (4)$$

where δ is the magnitude of the strain. Then the strain energy is expressed as [13];

$$E(\delta) = E(0) + 6C_sV_0\delta^2 + O(\delta^3), \quad (5)$$

where $E(0)$ is the unstrained ground state energy of the system and V_0 is its volume. C_{44} is calculated using following strain tensor which produces an orthorhombic distortion.

$$\epsilon = \begin{pmatrix} 0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix}. \quad (6)$$

Then the strain energy is:

$$E(\delta) = E(0) + 2C_{44}V_0\delta^2 + O(\delta^4) \quad (7)$$

C_{44} and C_s are obtained from the fitting parameters of Eqs. (5) and (7) and other elastic constants are calculated from shear constant C_s and bulk modulus B.

Exchange-correlation potential was approximated with GGA (Generalized Gradient Approximation) functionals of the Density Functional Theory (DFT) with Perdew–Burke–Ernzerhof parameterization [14]. GGA is more successful to describe the physical properties of metals with increasing complexity of Fermi surface and increasing deviation from homogeneous electron gas. Pseudopotentials are generated by scalar relativistic calculation for La and Bi and non-relativistic calculation for N atoms with non-linear core correction. Brillouin zone integration was performed with automatically generated $16 \times 16 \times 16$ k-point mesh following the convention of Monkhorst and Pack [15]. Wave-functions were expanded in plane wave basis sets up to a kinetic energy cut-off value of 950 eV. Methfessel-Paxton type smearing was applied on fermionic occupation function with $\sigma = 0.25$ eV smearing parameter [16]. Spin-orbit interactions were not included in the calculation procedure.

Phonon dispersion spectra was constructed using Density Functional Perturbation Theory (DFPT) in the linear response approach [17–19]. This method enables one to calculate the vibrational properties of materials with high level of accuracy. A relatively higher kinetic energy cut-off value with 1220 eV was used for phonon calculation in order to obtain better accuracy. The energy threshold value for convergence was 1.0×10^{-14} Ry. Dynamical matrices were calculated in a uniform grid of $4 \times 4 \times 4$ k-points in the irreducible part of the Brillouin zone. Then full phonon dispersion spectra can be obtained with Fourier transform using dynamical matrices.

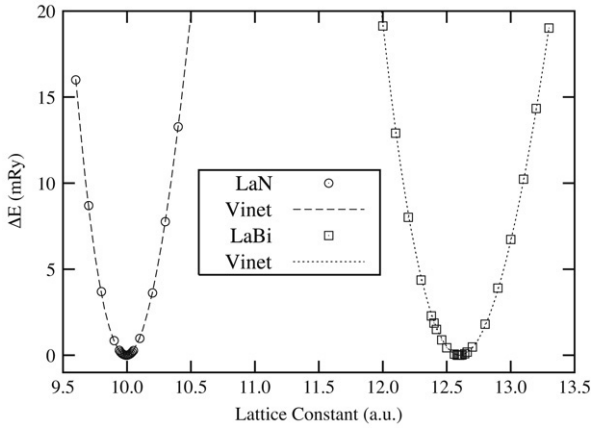

Fig. 1. Energy difference due to stable state vs lattice constant for LaN and LaBi systems and fit curves according to Vinet equation of states.

3. Results and discussion

3.1. Elastic properties

In Fig. 1, the calculated total energy values with respect to lattice constant were shown for LaN and LaBi systems. The stable state lattice constants for LaN and LaBi structures are 9.99 and 12.60 a.u., respectively. These values have been fitted to Vinet equation of states to get zero pressure bulk modulus and its pressure derivatives. The calculated bulk moduli values are 119.7 and 47.8 GPa for LaN and LaBi single crystals, respectively. The experimental lattice constants values of LaN and LaBi systems were determined as 10.01 a.u. and 12.40 a.u., respectively [20,21]. The experimental bulk modulus value for LaBi system is 55 GPa [21] and was calculated as 50.03 [11] and 65.18 GPa [22] in previous theoretical studies. Our bulk moduli values were also checked with Murnaghan [23] equation of states and almost the same values with ∼2 GPa deviations were obtained.

The energy differences due to undistorted cubic cell vs magnitude of the strains and fit curves are shown in Fig. 2. The range of strain magnitude δ was chosen as $(-0.05, 0.05)$ in which range Hook's law is well obeyed and harmonicity is conserved. The first order terms in energy due to initial hydrostatic pressure are eliminated by the utilization of isochoric strains. The system was relaxed after each distortion in order to reach the equilibrium state with negligible forces on the atoms. Calculated elastic coefficients have high accuracy due to very low asymptotic errors in fitting process with less than 0.1%. All calculated structural and elastic parameters of LaN and LaBi systems are shown in Table 1 together with other available theoretical and experimental data. There is no information about the elastic parameters of LaN compound in the literature. Hence we cannot compare these values due to the absence of any theoretical or experimental study. Ultrasound velocities were directly calculated from elastic constants using well known Christoffel equations [24] of the theory of elasticity: $\upsilon_L = \sqrt{C_L/\rho}$, $\upsilon_{TA1} = \sqrt{C_{44}/\rho}$, and $\upsilon_{TA2} = \sqrt{C_s/\rho}$, in which calculated lattice constants and densities were used ($\rho_{\mathrm{LaN}} = 6.845\,\mathrm{g/cm^3}$, $\rho_{\mathrm{LaBi}} = 7.761\,\mathrm{g/cm^3}$). L, TA_1, and TA_2 subscripts stand for longitudinal and two transverse acoustic waves, respectively. The elastic modulus C_L is expressed as: $C_L = (C_{11} + C_{12} + 2C_{44})/2$. The accuracy of ultrasound velocities is as high as elastic constants values.

The important information about the structural stability of crystalline solids is incorporated into elastic parameters. The Zener elastic anisotropy ratio is defined as $A = 2C_{44}/(C_{11} - C_{12})$. Elastic anisotropy factor for LaN and LaBi systems are 1.04 and 0.32, respectively. Most rare-earth monopnictides have approximately

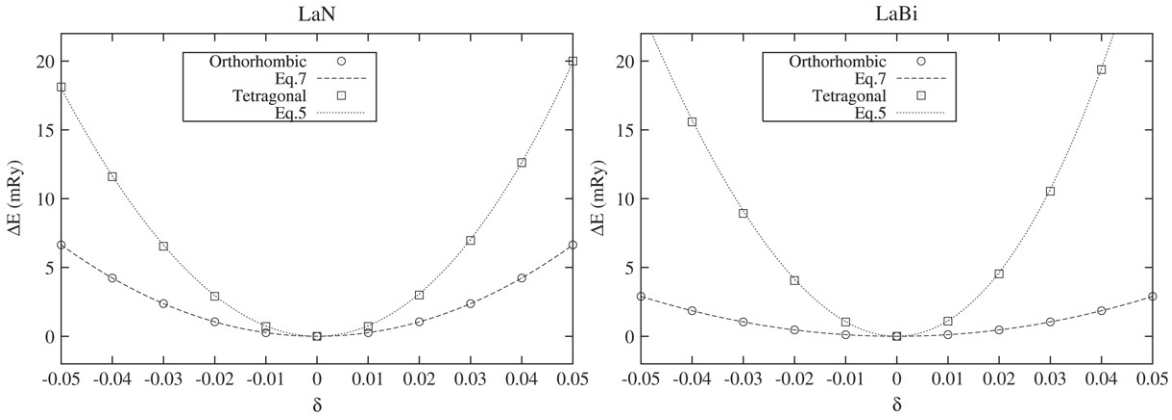

Fig. 2. Energy difference due to undistorted cubic cell vs magnitude of strain and fit curves for LaN and LaBi systems.

Table 1
Calculated and available experimental and theoretical values of lattice constant, bulk modulus, elastic stiffness constants and ultrasound velocities (propagating in the [110] direction) of LaN and LaBi crystals in rock salt structure

		a (a.u.)	B (GPa)	B'	C_s (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	υ_{TA1} (km/s)	υ_{TA2} (km/s)	υ_L (km/s)
LaN	Present	9.99	119.7	4.39	74.6	219.2	70.0	77.5	3.36	3.30	5.70
	Present	12.60	47.8	3.95	53.9	119.7	11.9	17.1	1.48	2.64	3.27
LaBi	Exp.	12.40[a]	55.0[b]	–	–	–	–	–	–	–	–
	Theo.	12.08[b]	50.03[c]	5.46[c]	–	109.6[c]	18.9[c]	18.9[c]	–	–	–

[a] Reference [21].
[b] Reference [22].
[c] Reference [11].

∼0.35 elastic anisotropy ratio [3,25]. The cerium pnictides, which is known as a group of pnictides showing various anomalous physical properties [26], have relatively higher elastic anisotropy ratios between 0.45 and 0.65 [27]. The larger values indicate the tendency to differ from cubic structures [28]. The much larger anisotropy value observed for LaN crystal is a strong clue for relatively high instability of LaN system as compared to other rare-earth monopnictides.

In a recent work, Pagare and Sanyal studied the elastic and structural properties and phase transitions of rare-earth bismuthides (REBi; RE:La, Ce and Pr) [11]. Their presented elastic constants for rock-salt LaBi slightly differ from our calculated ones. This difference is mainly due to the potential functions used. They used an empirical interatomic potential which is specially designed for investigating the high-pressure structural properties of rare-earth pnictides and chalcogenides, while ultrasoft pseudopotentials generated in GGA scheme were used in the present work. GGA functionals make an improvement over LDA in metallic systems and give relatively better results in comparison to other parameterizations. It is also known that the ground state stable electronic structure of several binary alloys can be better described by GGA functionals and experimental findings can be verified by high accuracy.

3.2. Phonon properties

The anomalous elastic behavior of LaN system is also seen in phonon dispersion spectra. The phonon dispersion curves of LaN and LaBi systems were shown in Fig. 3. Phonon dispersion spectra of LaN system contains large soft modes with negative frequencies in all main symmetry directions in BZ. In order to be sure about the observed vibrational anomaly, the phonon calculation of LaN system was also performed in direct force constant method with $2 \times 2 \times 2$ cubic supercell containing 16 atoms and 0.02 Å atomic displacement amplitude. Phonon softening is a direct indication of instability of a crystal structure. The physical properties of LaN compound in NaCl structure differ from all other lanthanum monopnictides. Almost all monopnictides in rock salt structure have metallic character under ambient temperature and pressure. But LaN structure has only a few electronic bands crossing the Fermi level yielding a very low electronic density of states around Fermi level as seen from Fig. 4, in which orbital projected partial electronic density of states for LaN and LaBi systems are shown. The main contributions to electronic density of states around Fermi level come from the La-3d states and 2p states of other pnictogen atom (N or Bi). The DOS values at Fermi level in units of states/eV are: La-3d = 0.008, N-2p = 0.111 in LaN and La-3d = 0.144, Bi-2p = 0.107 in LaBi structures. Note that, the contributions of the pnictogen atom are very close for both systems, but the contributions of La change remarkably between different structures. Clearly, LaN compound has a weaker metallic property in comparison to other rare-earth monopnictides. La-3d states show a much stronger hybridization with other high energy electronic states in LaN system. Consequently, La-3d states cover an extremely large energy range especially above the Fermi level. The structural instability obtained might be caused by anharmonic effects of strong electron–phonon coupling resulting a completely unstable cubic configuration. The radius of Bi ion is much larger than the N ion and LaBi system has partially filled f-states as a different case from LaN structure. But the densities of f-electronic states are very low about Fermi level and become remarkable about 14 eV energy levels. The mixing of p- and f-like states in LaBi can have effect on physical properties of this compound.

Hasegawa stated that LaN has the widest 4f bands among the other lanthanum pnictides [10]. He also mentioned that La-5p bands in LaN can affect valance band. This situation is also a consequence of low lattice constant value of LaN. In that work, electronic band structure of LaN was semi-metallic with slight overlap of bands and very low density of states at Fermi level. Vaitheeswaran et al. reported a comprehensive study on structural phase stability of LaN investigated by TB-LMTO method. They studied NaCl and CsCl phases and found NaCl structure stable

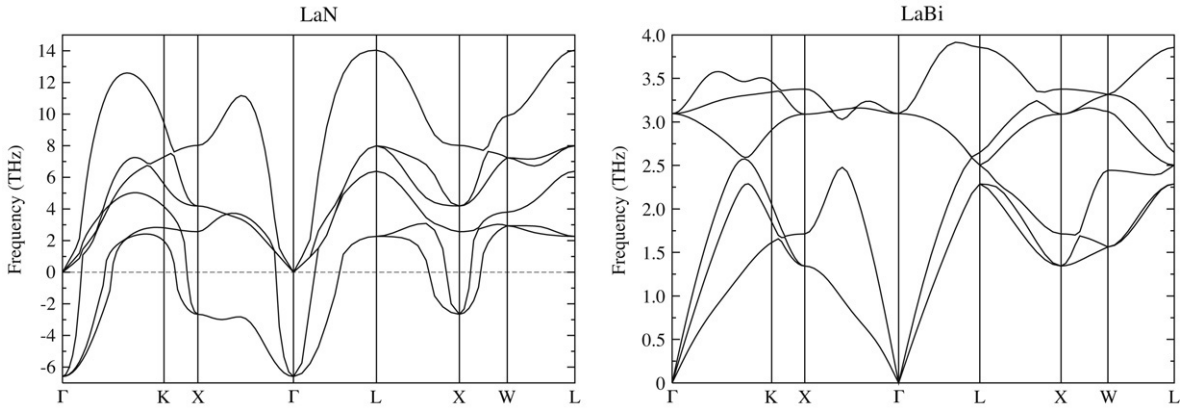

Fig. 3. Phonon dispersion curves for LaN and LaBi systems along the main symmetry directions in BZ.

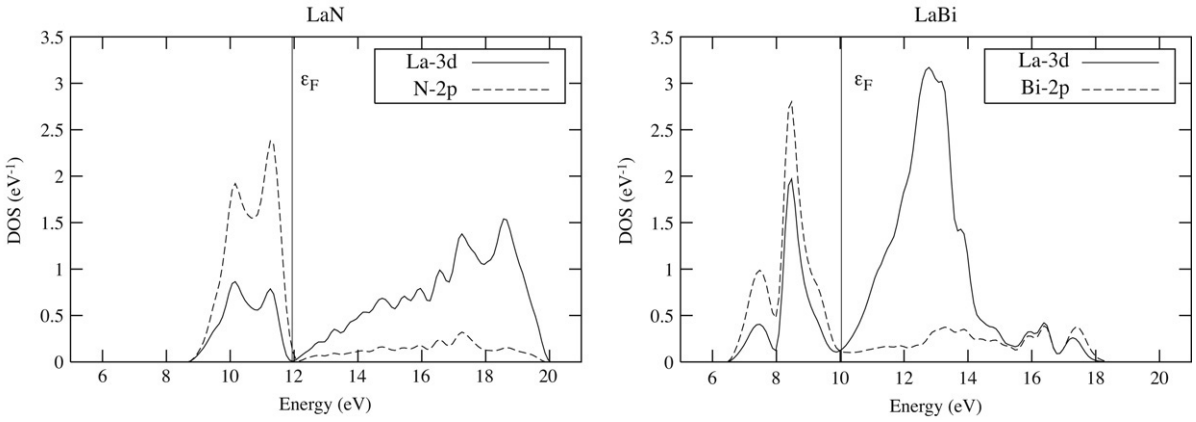

Fig. 4. The orbital projected electronic density of states of LaN and LaBi compounds.

under ambient conditions. They also mentioned the high level hybridization of La-d and N-p states in view of electronic density of states. In another study, LaBi and LaSb compounds were studied by the TB-LMTO method within the LDA scheme [22]. According to electronic band structure in that study, p-like states hybridizes with La-s and d-like states. These bands lie above the Fermi level and cause different physical properties of these compounds in comparison to other rare-earth pnictides.

The big difference in frequency scale of phonon dispersions of LaN and LaBi systems are mainly due to very large atomic mass difference of pnictogen atoms ($M_N = 14.00$, $M_{Bi} = 208.98$). The full phonon dispersion curve of LaBi system is similar to LaSb given in Ref. [3] and typical for lanthanum monopnictides. The energy of the longitudinal acoustic (LA) mode is almost the same as the transverse optical (TO) branch at $\frac{2\pi}{a}[0.55\ 0.55\ 0]$ **q**-point along the Γ–K direction. The energy of the LA branch becomes higher than the TO mode at L point. There is a visible gap between acoustic and optical modes along the [100] direction. Along this direction, the frequencies of the two overlapped transverse optical mode are almost constant about 3.05–3.10 THz, while longitudinal optical (LO) branch shows dispersive behavior. The energy of the LO mode is always higher than the other modes along the all symmetry directions and it becomes maximum at $\frac{2\pi}{a}[0.35\ 0.35\ 0.35]$ **q**-point in the Γ–L direction. No vibrational anomaly was observed in overall phonon spectra of LaBi in our study and for most lanthanum monopnictides in other theoretical works.

The ultrasound velocities (propagating in the Γ–K direction) for LaBi system were also calculated using the initial slopes ($\mathbf{q} \to 0$) of the phonon dispersion curves near Γ point and determined as: $\upsilon_{TA1} = 1.47$ km/s, $\upsilon_{TA2} = 2.36$ km/s, and υ_L=3.22 km/s. These values are in very good agreement with the values given in Table 1 which are directly calculated from elastic constants. This situation also approves the accuracy of the calculated elastic constants values.

4. Summary

In this study, we have investigated the elastic and phonon properties of two lanthanum monopnictides compounds, LaN and LaBi by *ab initio* calculations in the framework of the Density Functional Theory. The vibrational properties were studied in the linear response approach. The second order elastic stiffness coefficients are calculated using tetragonal and orthorhombic distortions on cubic rock salt structure. There is a few theoretical or experimental study on the elastic properties of these compounds in the literature, but the calculated values should be highly accurate due to very low errors obtained in the whole calculation process. A large structural instability characterized by large softening of phonon spectra and large elastic anisotropy was observed for LaN single crystal. The physical origins of the observed anomaly might be attributed to anharmonic effects of electron–phonon interactions in this system. Some anomalies in electronic structure of LaN were also reported in other theoretical studies. The electronic band structure of LaN differs from other lanthanum pnictides with very low states densities at Fermi level and slightly overlapping band with semi-metallic behavior. Large elastic anisotropy of LaN indicates the tendency to differ from cubic structure. Hence ground state stable structure of LaN may be a distorted cubic structure. LaBi system does not show any vibrational anomalous property in comparison to other rare earth monopnictides indicating a stable low pressure phase (NaCl structure).

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References

[1] G. Vaitheeswaran, V. Kanchana, M. Rajagopalan, J. Alloys Compd. 336 (2002) 46.
[2] I. Shirotani, K. Yamanashi, J. Hayashi, N. Ishimatsu, O. Shimomura, T. Kikegawa, Solid State Commun. 127 (2003) 573.
[3] H.M. Tütüncü, S. Bağci, G.P. Srivastava, J. Phys. Condens. Matter. 19 (2007) 156207.
[4] C.G. Olsen, P.J. Benning, M. Schmidt, D.W. Lynch, P. Canfield, D.M. Wieliczka, Phys. Rev. Lett. 76 (1996) 4265.
[5] M. Yoshida, K. Koyama, T. Tomimatsu, M. Shirakawa, A. Ochiai, M. Motokawa, J. Phys. Soc. Japan 70 (2001) 2078.
[6] A. Svane, Z. Szotek, W.M. Temmerman, H. Winter, Solid State Commun. 102 (1997) 473.
[7] G. Pagare, S.P. Sanyal, P.K. Jha, J. Alloys Compd. 398 (2005) 16.
[8] I. Shirotani, J. Hayashi, K. Yamanashi, K. Hirano, T. Adachi, N. Ishimatsu, O. Shimomura, T. Kikegawa, Physica B 334 (2003) 167.
[9] G. Vaitheeswaran, V. Kanchana, M. Rajagopalan, Solid State Commun. 124 (2002) 97.
[10] A. Hasegawa, J. Phys. C: Solid State Phys. 13 (1980) 6147.
[11] G. Pagare, S.P. Sanyal, Phase Transitions 79 (2006) 935.
[12] P. Vinet, J. Ferrante, J.R. Smith, J.H. Rose, J. Phys. C 19 (1986) L467.
[13] O. Gülseren, R.E. Cohen, Phys. Rev. B 65 (2002) 064103.
[14] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[15] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[16] M. Methfessel, A.T. Paxton, Phys. Rev. B 40 (1989) 3616.
[17] X. Gonze, Phys. Rev. A 52 (1995) 1086.
[18] X. Gonze, Phys. Rev. A 52 (1995) 1096.
[19] S. Baroni, S. de Gironcoli, A.D. Corso, Rev. Modern. Phys. 73 (2001) 515.
[20] R.W.G. Wyckoff, Crystal Structures, 2nd edition, vol 1, Wiley, London, 1963, 87.
[21] U. Benedict, S. Dabos-Seignon, J.P. Dancausse, M. Gensini, L. Gerward, R.G. Haire, J. Alloys Compd. 181 (1992) 1.
[22] G. Vaitheeswaran, V. Kanchana, M. Rajagopalan, Physica B 315 (2002) 64.
[23] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 50 (1944) 697.
[24] E.B. Christoffel, Ann. Mat. Pura Appl. 8 (1877) 193.
[25] V. Srivastava, S.P. Sanyal, J. Alloys Compd 366 (2004) 15.
[26] A. Svane, Z. Szotek, W.M. Temmerman, J. Laegsgaard, H. Winter, J. Phys. Condens. Matter. 10 (1998) 5309.
[27] V. Srivastava, A.K. Bandyopadhyay, P.K. Jha, S.P. Sanyal, J. Phys. Chem. Solids 64 (2003) 907.
[28] S.Q. Wang, H.Q. Ye, J. Phys. Condens. Matter. 15 (2003) 5307.